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(54) **Hair dye composition**

Haarfärbezusammensetzung

Composition pour teindre la chevelure

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**US-A- 3 741 982** **US-A- 3 812 107**  
**US-A- 3 897 418** **US-A- 4 168 144**  
**US-A- 4 344 879** **US-A- 5 593 459**

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**EP 1 142 559 B1**

**Description****Technical Field**

5 [0001] The present invention relates to a hair dye composition which has markedly high dyeing power, can impart the hair with a vivid color ranging from yellow to orange, has less color fade over time and undergoes a smaller change in the color tone of the dye even after storage.

**Background Art**

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[0002] Hair dyes can be classified by the dye to be used therefor, or whether they have bleaching action of melanin or not. Typical examples include a two-part permanent hair dye composed of a first part containing an alkali agent, an oxidation dye and a direct dye such as nitro dye and a second part containing an oxidizing agent; and one-part semi-permanent hair dye containing an organic acid or an alkali agent, and a direct dye such as acid dye, basic dye or nitro dye.

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[0003] The above-described permanent hair dye is however accompanied with the drawbacks that color tone imparted by an oxidation dye is not so vivid and the color of the hair dyed with a vivid-color producing nitro dye ordinarily employed as a direct dye markedly fades over time and becomes dull soon even if the color tone rightly after dyeing is very vivid (Japanese Patent Application Laid-Open (*Kokai*) No. Hei 6-271435).

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[0004] Recently, hair dyes containing as a direct dye a so-called cationic dye having a cation group contained in their conjugate system have been reported (Japanese Language Laid-Open Publication (PCT) No. Hei 8-507545, 8-501322 or 10-502946, or Japanese Patent Application Laid-Open (*Kokai*) No. Hei 10-194942). They have been found to involve drawbacks that intended dyeing effects are not available owing to decomposition of them caused by mixing, upon hair dyeing, with hydrogen peroxide ordinarily employed as an oxidizing agent; and that when a cationic group is contained in an azo(-N=N-)-based conjugated system, they are unstable to an alkali agent or a reducing agent essentially contained in a permanent hair dye.

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**Disclosure of the Invention**

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[0005] An object of the present invention is to provide a hair dye composition which has high hair dyeing power, has less color fade over time, and undergoes only a smaller change in color tone of the dye after storage, therefore has excellent stability.

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[0006] The present inventors have found that a hair dye composition containing the below-described compound - which is known as a cationic dye for dyeing or printing therewith fiber materials, paper or leather and is, for example, described in Japanese Patent Application Laid-Open (*Kokai*) No. Sho 53-12931, Sho 54-7425, Sho 54-127433 or Sho 56-76457 is named as Basic Yellow 21 or Basic Yellow 28 - can impart the hair with a vivid color ranging from yellow to orange without decomposing the dye upon hair drying, exhibits excellent light resistance, washing resistance, perspiration resistance, friction resistance and heat resistance, and undergoes a smaller change in the color tone of the dye after storage as compared with that rightly after preparation because the dye exists in the composition stably.

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[0007] In one aspect of the present invention, there is thus provided a hair dye composition comprising, as a direct dye, a compound represented by the following formula (1):

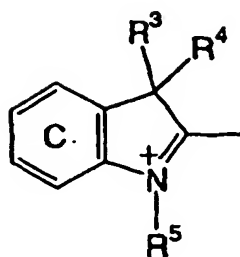


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[wherein, A represents a group of the following formula (2):

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(2)

(in which,  $R^3$ ,  $R^4$  and  $R^5$  each independently represents a  $C_{1-6}$  alkyl group which may have a substituent, ring C may have a substituent or may be cyclocondensed with an aromatic ring)

B represents an aromatic group which may have a substituent,

$R^1$  represents a hydrogen atom or a  $C_{1-6}$  alkyl group which may have a substituent,

$R^2$  represents a hydrogen atom or a  $C_{1-6}$  alkyl group which may have a substituent or an aromatic group which may have a substituent, or may form a heterocycle together with the carbon atom of the aromatic ring B, and

$X^-$  represents an anion.]

and an oxidizing agent.

[0008] In another aspect of the present invention, there is also provided a hair dyeing method which comprises applying the above-described hair dye composition to the hair.

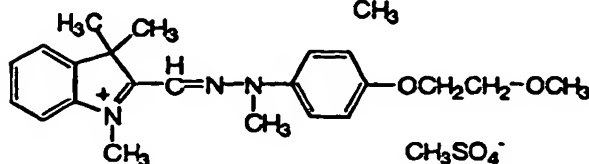
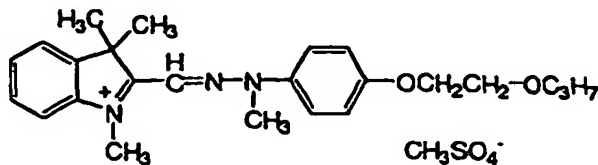
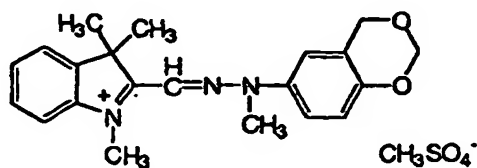
#### Best Mode for Carrying out the Invention

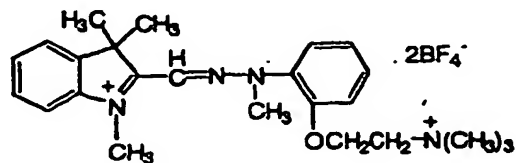
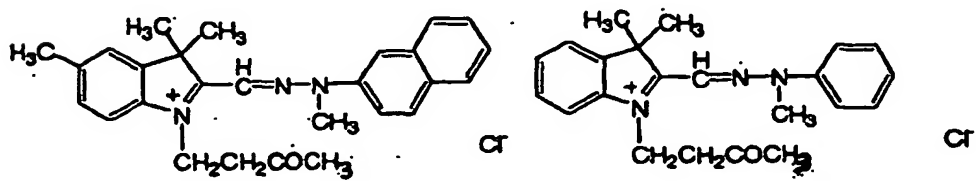
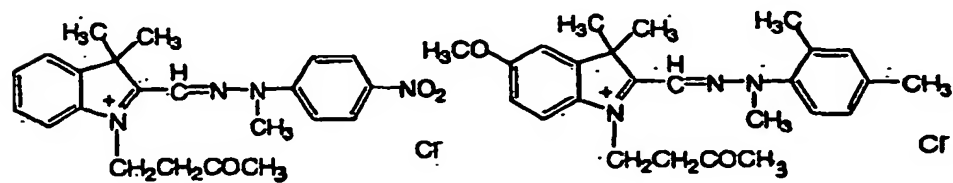
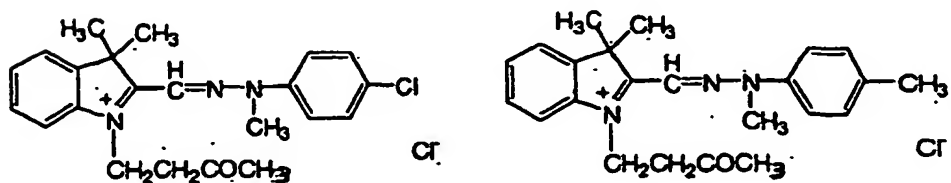
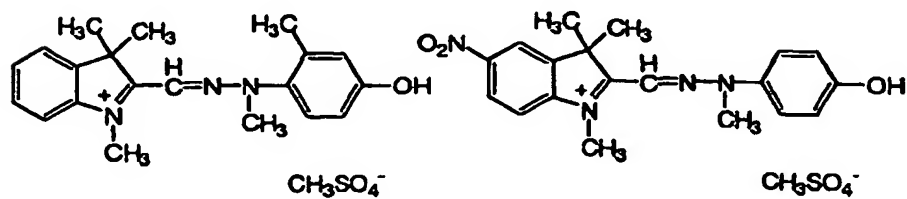
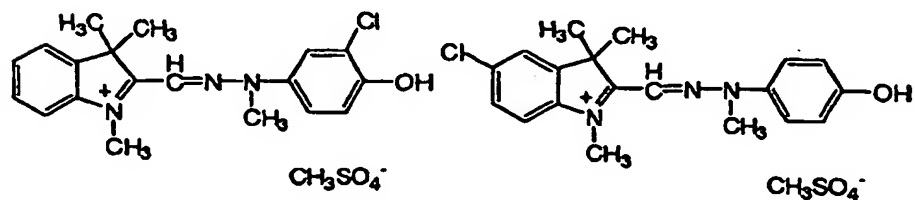
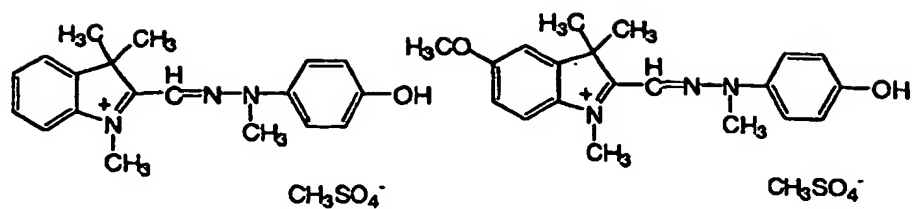
[0009] In the formulas (1), (2), examples of the  $C_{1-6}$  alkyl group as  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  or  $R^5$  include methyl, ethyl, propyl, isopropyl and cyclohexyl groups, which may each be substituted with an aryl, alkoxy, amino, hydroxyl or cyano group, or a halogen atom.

[0010] In the formula (1), examples of the substituent for the aromatic group as B or  $R^2$  or for the ring C include alkyl, aryl, alkoxy, amino, dialkylamino, hydroxyl, cyano and nitro groups and halogen atoms, more specifically, methyl, ethyl, methoxy, ethoxy and diethylamino groups and chlorine and bromine atoms. The substituent for B may be cationic and a trimethylammonium ethoxy group may be mentioned as an example.

[0011] In the formula (1), examples of the anion as  $X^-$  include chloride ions, bromide ions, iodide ions, trichlorozincic acid ions, tetrachlorozincic acid ions, sulfuric acid ions, hydrosulfuric acid ions, methyl sulfate ions, phosphoric acid ions, formic acid ions and acetic acid ions.

[0012] Specific examples of the direct dye (1) to be used in the present invention include the following compounds:





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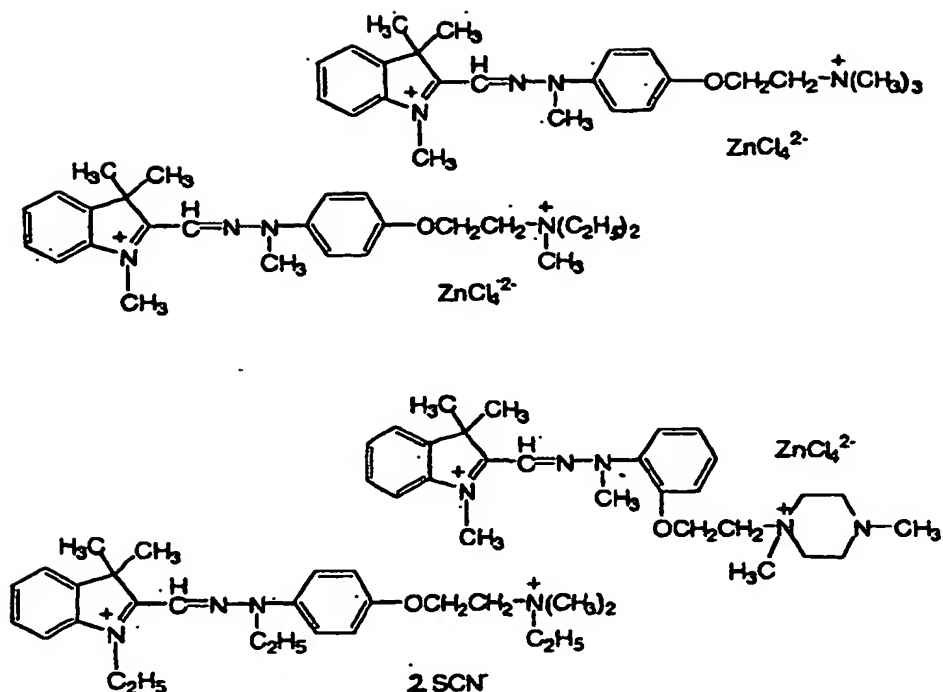
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[0013] As the direct dye (1), one or more can be used. Alternatively, another direct dye can be used in combination. Combination of the direct dye (1) with red and blue dyes makes it possible to dye the hair with a deep and highly lustrous dark brown or black color.

[0014] Examples of the direct dye other than the direct dyes (1) include Basic Blue 7 (C.I. 42595), Basic Blue 26 (C.I. 44045), Basic Blue 99 (C.I. 56059), Basic Violet 10 (C.I. 45170), Basic Violet 14 (C.I. 42515), Basic Brown 16 (C.I. 12250), Basic Brown 17 (C.I. 12251), Basic Red 2 (C.I. 50240), Basic Red 22 (C.I. 11055), Basic Red 76 (C.I. 12245), Basic Red 118 (C.I. 12251:1) and Basic Yellow 57 (C.I. 12719); and basic dyes as described in Japanese Patent Publication No. Sho 58-2204, Japanese Patent Application Laid-Open No. Hei 9-118832, Japanese Language Laid-Open Publication (PCT) No. Hei 8-501322 or Japanese Language Laid-Open Publication (PCT) No. Hei 8-507545.

[0015] The direct dye (1) is preferably added in an amount of 0.01 to 20 wt.%, more preferably 0.05 to 10 wt.%, especially 0.1 to 5 wt.% based on the whole composition (after mixture of all the parts when a two part or three part composition is employed; this will apply equally hereinafter). When another direct dye is added in combination, the content of it in total with the direct dye (1) preferably ranges from 0.05 to 10 wt.%, especially 0.1 to 5 wt.%.

[0016] The hair dye composition of the present invention is preferably adjusted to pH 6 to 11, with pH 8 to 11 being especially preferred. Examples of the alkali agent to be used for pH adjustment include ordinarily employed ones such as ammonia, organic amines and salts thereof. The alkali agent is preferably added in an amount of 0.01 to 20 wt.%, more preferably 0.1 to 10 wt.%, especially 0.5 to 5 wt.% based on the whole composition.

[0017] In the hair dye composition of the present invention, an oxidizing agent is incorporated. Thus, hair dyeing and bleaching can be carried out simultaneously, which facilitates more vivid hair dyeing. Ordinarily employed oxidizing agents, for example, hydrogen peroxide, persulfates such as ammonium persulfate, potassium persulfate and sodium persulfate, perborates such as sodium perborate, percarbonates such as sodium percarbonate and bromates such as sodium bromate and potassium bromate are usable. Out of them, hydrogen peroxide is especially preferred. The oxidizing agent is added in an amount of 0.5 to 10 wt.%, especially 1 to 8 wt.%, based on the whole composition.

[0018] In the hair dye composition of the present invention, an oxidation dye can be incorporated further. This incorporation enables markedly vivid dyeing not attainable by the single use of an oxidation dye. The above-exemplified oxidizing agents can be used as the oxidizing agent, with hydrogen peroxide being particularly preferred. Alternatively, an oxidizing enzyme such as laccase can be employed. For the oxidation dye, known color developers and couplers ordinarily employed for an oxidation type hair dye can be used.

[0019] Examples of the developer include p-phenylenediamines having one or several groups selected from  $\text{NH}_2$ -,  $\text{NHR}$ - and  $\text{NR}_2$ -groups (in which, R represents a  $\text{C}_{1-4}$  alkyl or hydroxyalkyl group) such as p-phenylenediamine, p-toluylenediamine, N-methyl-p-phenylenediamine, chloro-p-phenylenediamine, 2-(2'-hydroxyethylamino)-5-aminotoluene, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-hydroxyethyl-p-phenylenediamine, 2,6-dimethyl-p-phenylenediamine, methoxy-p-phenylenediamine, 2,6-dichloro-p-phenylenediamine, 2-chloro-6-methyl-p-phenylenediamine,

6-methoxy-3-methyl-p-phenylenediamine, 2,5-diaminoanisole, N-(2-hydroxypropyl)-p-phenylenediamine and N-2-methoxyethyl-p-phenylenediamine; 2,5-diaminopyridine derivatives and 4,5-diaminopyrazole derivatives, p-aminophenols such as p-aminophenol, 2-methyl-4-aminophenol, N-methyl-p-aminophenol, 3-methyl-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol and 2,5-dimethyl-4-aminophenol; o-aminophenols, o-phenylenediamines, 4,4'-diaminophenylamine and hydroxypropylbis(N-hydroxyethyl-p-phenylenediamine); and salts thereof.

[0020] Examples of the coupler include 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 5-amino-2-methylphenol, 5-(2'-hydroxyethylamino)-2-methylphenol, 2,4-diaminoanisole, m-toluylenediamine, resorcin, m-phenylenediamine, m-aminophenol, 4-chlororesorcin, 2-methylresorcin, 2,4-diaminophenoxyethanol, 2,6-diaminopyridine, 2-amino-3-hydroxypyridine, 4-hydroxyindole, 6-hydroxyindole, 2,4-diamino-6-hydroxypyrimidine, 2,4,6-triaminopyrimidine, 2-amino-4,6-dihydroxypyrimidine, 4-amino-2,6-dihydroxypyrimidine, 4,6-diamino-2-hydroxypyrimidine and 1,3-bis(2,4-diaminophenoxy)propane; and salts thereof.

[0021] As the developer or coupler, they may be used either singly or in combination. Each of the developer and coupler is added in an amount of 0.01 to 20 wt.%, especially 0.5 to 10 wt.% based on the whole composition.

[0022] To the hair dye composition of the present invention, a known autoxidation dye typified by an indole or an indoline, or a known direct dye such as a nitro dye or a disperse dye can also be added.

[0023] When an anionic component (such as anionic surfactant or anionic polymer) is added to the hair dye composition of the present invention, it is preferred to satisfy the following equation:

$$\frac{\text{"Ion activity concentration of the anionic component}}{\text{ion activity concentration of the cationic direct dye (1)}} \leq 8$$

The term "ion activity concentration" as used herein means "molar concentration x ionic valence"

[0024] Addition of a polyol, polyol alkyl ether, cationic or amphoteric polymer or silicone to the hair dye composition of the present invention is preferred for uniform hair dyeing and improvement in cosmetic effects.

[0025] In addition to the above-described components, those ordinarily employed as a raw material for cosmetics can be added to the hair dye composition of the present invention within an extent not impairing the advantages of the present invention. Examples of such an optional component include hydrocarbons, animal or vegetable fats and oils, higher fatty acids, organic solvents, penetration promoters, cationic surfactants, natural or synthetic polymers, higher alcohols, ethers, amphoteric surfactants, nonionic surfactants, protein derivatives, amino acids, antiseptics, chelating agents, stabilizing agents, antioxidants, plant extracts, crude drug extracts, vitamins, colorants, perfumes and ultraviolet absorbers.

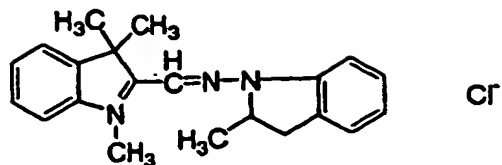
[0026] The hair dye composition of the present invention can be prepared in a conventional manner into a one-part composition, a two-part composition having a first-part component containing an alkali agent and a second-part component containing an oxidizing agent, or a three-part composition containing, in addition to these two components, a powdery oxidizing agent such as persulfate. The direct dye (1) can be incorporated in either one or both of these components of the two-part or three-part composition. The one-part type is applied to the hair directly, while the two- or three-part type is applied to the hair after mixing these parts upon hair dyeing.

[0027] No particular limitation is imposed on the form of the hair dye composition of the present invention. Examples include powder, transparent liquid, emulsion, cream, gel, paste, aerosol, and aerosol foam. It preferably has a viscosity of 2000 to 100000 mPa·s in the stage of application to the hair (after mixing of all the components when a two-part or three-part type is employed).

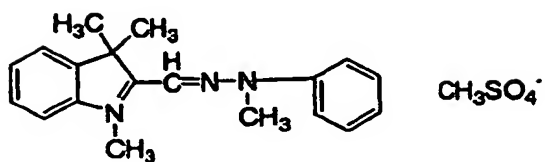
-Examples-

[0028] Compounds employed in the below-described examples are as follows:

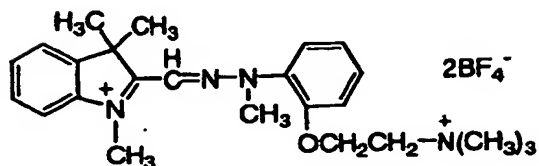
## Compound (a)



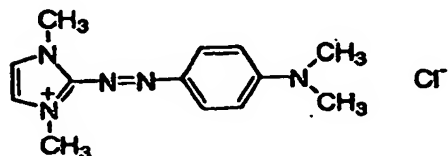
## Compound (b)



## Compound (c)



## Compound (d)



Examples 1 to 5 (Reference Examples)

[0029] In a manner known per se in the art, hair dye compositions as shown in Table 1 were prepared.

Table 1

(wt.%)	Examples 3				
	1	2	3	4	5
Dye [Compound (a)]	0.2		0.15	0.1	
Dye [Compound (b)]		0.5		0.1	0.2
Dye [Compound (d)]			0.15	0.1	0.05
Dye [Basic Blue 7]			0.1	0.1	
Ethanol		5		5	5
Propylene glycol			5		5
Diethylene glycol monoethyl ether		10			
Guar gum	1				
Hydroxypropyl guar gum		1	1	1	1

### Examples 6 to 9

Table 2

(wt.%)		Examples			
		6	7	8	9
1st part	Dye [Compound (a)]	0.2		0.15	0.2
	Dye [Compound (b)]		0.1	0.15	
	Dye [Compound (d)]		0.1		0.05
	Dye [Basic Blue 99]		0.3		
	28 wt.% Aqueous ammonia	5			
	Monoethanolamine	2			
	Propylene glycol	8			
	Polyoxyethylene (20) isostearyl ether	24			
	Polyoxyethylene (2) isostearyl ether	20			
	"Merquat 280" (trade name; product of Calgon Corp., a 35 wt.% aqueous solution)	8			
	"Polymer JR400" (trade name; product of Union Carbide)		0.5		0.5
	"Amodimethicone SM8702C" (trade name; product of Dow Corning Toray Silicone)			2 2	
	"Polyether modified silicone KF6005" (trade name; product of Shin-Etsu Chemical)				0.3
	Tetrasodium ethylenediaminetetraacetate	0.1			
	Perfume	q.s.			
Ammonium chloride	Amount to adjust pH to 10				
Water	Balance				



Table 2 (continued)

(wt.%)		Examples			
		6	7	8	9
2nd part	35 wt.% Aqueous hydrogen peroxide	17.1			
	Methylparaben	0.1			
	Phosphoric acid	Amount to adjust pH to 3.5			
	Water	Balance			

Examples 10 to 12

[0031] In a manner known per se in the art, hair dye compositions as shown in Table 3 were prepared.

Table 3

(wt.%)		Examples		
		10	11	12
1st part	Toluene-2,5-diamine	1.9	1	
	Para-aminophenol			1
	Resorcin	2		
	Para-amino-ortho-cresol			1.1
	2,4-Diaminophenoxyethanol		1.37	
	Dye [Compound (a)]	0.05		
	Dye [Compound (b)]		0.15	
	Dye [Compound (c)]			0.1
	28wt.% Aqueous ammonia	5		
	Monoethanolamine	2		
	Propylene glycol	8		
	Polyoxyethylene (20) isostearyl ether	24		
	Polyoxyethylene (2) isostearyl ether	20		
	"Merqual 280" (trade name; product of Calgon Corp., a 35 wt.% aqueous solution)	8		
	"Polymer JR400" (trade name; product of Union Carbide)		0.5	
	"Arnodimethicone SM8702C" (trade name; product of Dow Corning Toray Silicone)			2
	Sodium sulfite	0.05		
	Ascorbic acid	0.5		
	Tetrasodium ethylenediaminetetraacetate	0.1		
	Perfume	q.s.		
	Ammonium chloride	Amount to adjust pH to 10		
	Water	Balance		

Table 3 (continued)

(wt.%)		Examples		
		10	11	12
5 10	2nd part	35 wt.% Aqueous hydrogen peroxide		
		17.1		
		Methylparaben		
		0.1		
		Phosphoric acid		
		Amount to adjust pH to 3.5		
		Water		
		Balance		

## Example 13

[0032] In a manner known per se in the art, the following hair dye composition was prepared.

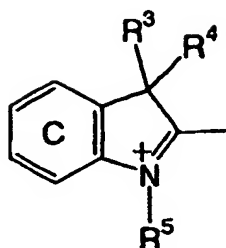
(First part)	(wt.%)
Para-aminophenol	1
Para-amino-ortho-cresol	1.1
Compound (a)	0.1
28 wt.% Aqueous ammonia	5
Monoethanolamine	2
Cetanol	8.5
Polyoxyethylene (40) cetyl ether	3
Polyoxyethylene (2) cetyl ether	3.5
Stearyl trimethyl ammonium chloride	2
Liquid paraffin	0.5
Sodium sulfite	0.05
Ascorbic acid	0.5
Tetrasodium ethylenediaminetetraacetate	0.1
Perfume	q.s.
Ammonium chloride	Amount to adjust pH to 10
Water	Balance
(Second part)	(wt.%)
35 wt.% Aqueous hydrogen peroxide	17.1
Methylparaben	0.1
Phosphoric acid	Amount to adjust pH to 3.5
Water	Balance

## Claims

1. A hair dye composition comprising, as a direct dye, a compound represented by the following formula (1):



[wherein, A represents a group of the following formula (2):



(2)

(wherein,  $R^3$ ,  $R^4$  and  $R^5$  each independently represents a  $C_{1-6}$  alkyl group which may have a substituent, ring C may have a substituent or may be cyclocondensed with an aromatic ring)

B represents an aromatic group which may have a substituent,

$R^1$  represents a hydrogen atom or a  $C_{1-6}$  alkyl group which may have a substituent,

$R^2$  represents a hydrogen atom or a  $C_{1-6}$  alkyl group which may have a substituent or an aromatic group which may have a substituent or may form a heterocycle together with the carbon atom of the aromatic ring B, and

$X^-$  represents an anion.] and  
an oxidizing agent.

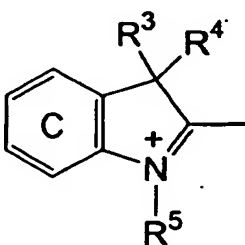
2. A hair dye composition according to claim 1, further comprising an oxidation dye.
3. A hair dyeing method, which comprises applying a hair dye composition according to claim 1 or 2 to the hair.

#### Patentansprüche

1. Haarfarbstoffzusammensetzung, umfassend als einen direkten Farbstoff eine Verbindung, dargestellt durch die folgende Formel (1):



worin A eine Gruppe der folgenden Formel (2) darstellt:



(2)

worin  $R^3$ ,  $R^4$  und  $R^5$  unabhängig voneinander eine  $C_{1-6}$ -Alkylgruppe darstellen, die einen Substituenten haben kann, Ring C einen Substituenten haben kann oder mit einem aromatischen Ring cyclocondensiert sein kann, B eine aromatische Gruppe darstellt, die einen Substituenten haben kann,  $R^1$  ein Wasserstoffatom oder eine  $C_{1-6}$ -Alkylgruppe darstellt, die einen Substituenten haben kann,  $R^2$  ein Wasserstoffatom oder eine  $C_{1-6}$ -Alkylgruppe, die einen Substituenten haben kann, oder eine aromatische Gruppe, die einen Substituenten haben kann, darstellt oder zusammen mit einem Kohlenstoffatom des aromatischen Rings B einen Heterocyclus bilden kann, und  $X^-$  ein Anion darstellt, und ein Oxidationsmittel.

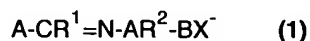
2. Haarfarbstoffzusammensetzung gemäß Anspruch 1, die weiterhin einen Oxidationsfarbstoff umfaßt.

3. Haarfärbungsverfahren, das die Anwendung einer Haarfarbstoffzusammensetzung gemäß Anspruch 1 oder 2 auf das Haar umfaßt.

## 5 Revendications

1. Composition de colorant pour les cheveux comprenant, en tant que colorant direct, un composé représenté par la formule (1) suivante :

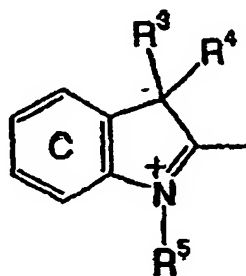
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[dans laquelle, A représente un groupe de la formule (2) suivante :

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(2)

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(dans laquelle, R<sup>3</sup>, R<sup>4</sup> et R<sup>5</sup> représentent chacun indépendamment un groupe alkyle en C<sub>1-6</sub> qui peut avoir un substituant, le cycle C peut avoir un substituant ou peut être cyclocondensé avec un cycle aromatique),

B représente un groupe aromatique qui peut avoir un substituant,

R<sup>1</sup> représente un atome d'hydrogène ou un groupe alkyle en C<sub>1-6</sub> qui peut avoir un substituant,

R<sup>2</sup> représente un atome d'hydrogène ou un groupe alkyle en C<sub>1-6</sub> qui peut avoir un substituant ou un groupe aromatique qui peut avoir un substituant ou peut former un hétérocycle avec l'atome de carbone du cycle aromatique B, et

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X<sup>-</sup> représente un anion.] et  
un agent oxydant.

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2. Composition de colorant pour les cheveux selon la revendication 1, comprenant en outre un colorant d'oxydation.

3. Procédé de coloration des cheveux, qui comprend l'application d'une composition de colorant pour les cheveux selon la revendication 1 ou 2 sur les cheveux.

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